

# Absence of charge order in the dimerized $\kappa$ -phase BEDT-TTF salts

Katrin Sedlmeier,<sup>1</sup> Sebastian Elsässer,<sup>1</sup> Rebecca Beyer,<sup>1</sup> Dan Wu,<sup>1</sup>  
Tomislav Ivek,<sup>1,2</sup> Silvia Tomić,<sup>2</sup> John A. Schlueter,<sup>3</sup> and Martin Dressel<sup>1</sup>

<sup>1</sup>*Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, D-70550 Stuttgart Germany*

<sup>2</sup>*Institut za fiziku, P.O. Box 304, HR-10001 Zagreb, Croatia*

<sup>3</sup>*Material Science Division, Argonne National Laboratory, Argonne, Illinois 60439-4831, U.S.A.*

(Dated: August 14, 2012)

Utilizing infrared vibrational spectroscopy we have investigated dimerized two-dimensional organic salts in order to search for possible charge redistribution that might cause electronic dipoles and ferroelectricity: the quantum spin liquid  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>, the antiferromagnetic Mott insulator  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl, and the superconductor  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br. None of them exhibit any indication of charge disproportionation upon cooling down to low temperatures. No modification in the charge distribution is observed around  $T = 6$  K where a low-temperature anomaly has been reported for the spin-liquid  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. In this compound the in-plane optical response and vibrational coupling are rather anisotropic, indicating that the tilt of the BEDT-TTF molecules in  $c$ -direction and their coupling to the anion layers has to be considered in the explanation of the electromagnetic properties.

PACS numbers: 71.30.+h, 75.10.Kt 74.70.Kn, 78.30.Jw

## I. INTRODUCTION

Electronic ferroelectricity and magneto-dielectric phenomena are one of the central issues in solid state physics in recent years due to fundamental questions as well as possible applications. It is extensively explored in inorganic transition metal oxides such as LuFe<sub>2</sub>O<sub>4</sub> or YbFe<sub>2</sub>O<sub>4</sub><sup>1,2</sup> as well as organic charge-transfer salts (TMTTF)<sub>2</sub>X.<sup>3,4</sup> An additional aspect is brought in by multiferroics, i.e. materials with coupled electric, magnetic, and structural order parameters that result in simultaneous ferroelectricity, ferromagnetism, and ferroelasticity.<sup>5,6</sup> While there are different scenarios realized by now,<sup>7,8</sup> here we focus on multiferroicity due to charge ordering, described in the seminal review by van den Brink and Khomskii.<sup>9</sup> In charge-driven ferroelectricity a large magneto-dielectric coupling and a fast polarization switching are expected, since the electric polarization is governed by electrons compared to ions in conventional ferroelectrics.<sup>10</sup>

These phenomena are well studied in one-dimensional organic TMTTF salts,<sup>11–14</sup> for which charge order was proven by NMR spectroscopy,<sup>15–18</sup> dielectric permittivity measurements,<sup>3,19–22</sup> Raman and infrared investigations,<sup>23–25</sup> thermal expansion,<sup>26</sup> and neutron scattering experiments.<sup>27</sup> Calculations based on the extended Hubbard Hamiltonian could reproduce the charge-ordered state.<sup>28,29</sup> The charge per molecule alternates along the stacking direction  $a$  between charge rich ( $\rho_0 + \delta$ ) and charge poor molecules ( $\rho_0 - \delta$ ). Recent ESR experiments strongly suggest that two inequivalent magnetic TMTTF chains coexist in the charge-ordered regime,<sup>30</sup> most probably due to the loss of translational invariance in the  $bc$ -plane. The increase of mosaicity around  $T_{CO}$  inferred by  $X$ -ray investigations supports the development of ferroelectric domains in the nanometer scale.<sup>31</sup>

As far as organic crystalline materials are concerned, the two-dimensional BEDT-TTF salts with quarter-filled conduction band, such as  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> and  $\theta$ -(BEDT-TTF)<sub>2</sub>RbZn(SCN)<sub>4</sub>, have been established as model compounds of charge order for theory<sup>28</sup> and experiment.<sup>32</sup> The possibility of charge-disproportionation in dimerized half-filled BEDT-TTF systems, is intensely debated for the last years,<sup>33–36</sup> with particular emphasis on the  $\kappa$ -phase salts,<sup>37</sup> which form a triangular lattice of dimerized BEDT-TTF molecules that is subject to frustration.<sup>38–41</sup> Frequencies of certain intramolecular vibration modes in BEDT-TTF crystals strongly depend on molecular charge, which makes optical spectroscopy one of the most sensitive local probes to investigate the charge distribution.<sup>42–47</sup> We have performed comprehensive in- and out-of-plane infrared measurements on  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br,  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl, and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. For none of these systems the molecular vibrational modes split upon cooling; and thus there is no indication of charge redistribution as the temperature is reduced. This result is seemingly at odds with significant dielectric relaxation found in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>,<sup>48,49</sup> which has recently been interpreted as a consequence of electronic ferroelectricity.<sup>50,51</sup>

## II. MATERIALS

Single crystals of the quasi-two-dimensional organic charge-transfer salts  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br (abbreviated  $\kappa$ -Br),  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl (called  $\kappa$ -Cl) and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> ( $\kappa$ -CN hereafter) were grown by standard electrochemical methods.<sup>52,53</sup> In the crystallographic  $\kappa$ -phase, conducting layers of cationic bis-(ethylenedithio)tetra-

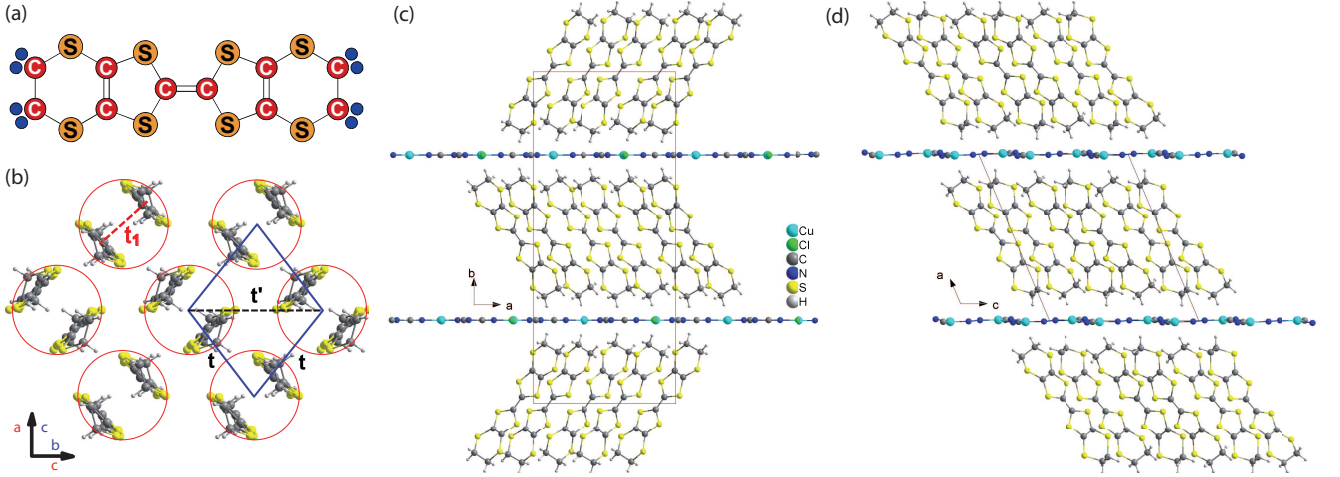


FIG. 1: (Color online) (a) Sketch of the bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF) molecule. (b) For  $\kappa$ -(BEDT-TTF)<sub>2</sub>X the molecules are arranged sideways in dimers (strongly coupled by  $t_1$ ), which constitute an anisotropic triangular lattice. The interdimer transfer integrals are labeled by  $t$  and  $t'$ . In the case of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl the plane is labeled as  $ac$  while it is the  $bc$ -plane in the case of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>, as denoted by the arrows. (c) The side view on  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl demonstrates the staggered layers of BEDT-TTF molecules separated by sheets of polymeric anions. (d) The Structure of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> consists of one layer tilted by  $\beta = 123^\circ$  at room temperature ( $125^\circ$  at low temperatures).<sup>41</sup>

thiafulvalene (BEDT-TTF) molecules are separated by essentially insulating anion sheets, as depicted in Fig. 1. The BEDT-TTF donors form face-to-face dimers which themselves are rotated by about  $90^\circ$  with respect to neighboring dimers, as sketched in Fig. 1(b).

$\kappa$ -CN crystallizes in a monoclinic structure (space group  $P2_1/c$ ) with the long axis of the BEDT-TTF molecules inclined by about  $25^\circ$  with respect to the layer normal,<sup>54</sup> as displayed in Fig. 1(d). For convention, in  $\kappa$ -CN the layer spans in the  $bc$ -plane and the  $a$ -axis points between the layers ( $a^*$  is normal to the  $bc$ -plane). The Cu<sub>2</sub>(CN)<sub>3</sub>-anions form a flat infinite two-dimensional network of copper and cyano groups in the  $bc$ -plane. In the case of isostructural compounds  $\kappa$ -Br and  $\kappa$ -Cl the polymeric anions consist of parallel infinite zigzag  $\cdots$  dicyanoamido-Cu(Cl/Br)-dicyanoamido  $\cdots$  chains running along the  $a$ -direction. The compounds form orthorhombic (space group  $Pnma$ ) two-layer systems (anion layers in  $ac$ -plane,  $b$ -axis perpendicular to it) with four (BEDT-TTF)<sub>2</sub> dimers per unit cell due to the tilting along  $a$  in opposite direction for adjacent layers, as displayed in Fig. 1(c).<sup>55,56</sup>

All three compounds are two-dimensional half-filled electron systems with considerably strong electronic correlations that places them close to a metal-insulator transition driven by effective electronic correlations  $U/t$ , where  $U$  is the on-site Coulomb repulsion and  $t$  the transfer integral. Due to the large orbital overlap,  $\kappa$ -Br is the organic superconductor with the highest transition temperature of 11.8 K at ambient pressure;<sup>55</sup> upon cooling it crosses over from a bad metal to a Fermi liquid around  $T_{\text{coh}} \approx 30$  K.<sup>57</sup> The sister compound  $\kappa$ -Cl is a Mott insu-

lator with antiferromagnetic order at low temperatures ( $T_N \approx 25$  K),<sup>58–60</sup> Applying a small amount of pressure (300 bar) reduces  $U/t$  sufficiently to cross the insulator-metal phase boundary (where it becomes superconducting at  $T_c = 12.8$ )<sup>56</sup> with unusual universality class of the critical phenomena at the pressure-driven Mott transition close to the critical endpoint.<sup>61</sup> Also chemical pressure by Br substitution is a tuning parameter to investigate the bandwidth-driven Mott insulator-metal transition.<sup>57,62</sup> For the Mott insulator  $\kappa$ -(BEDT-TTF)<sub>2</sub>-Cu<sub>2</sub>(CN)<sub>3</sub> hydrostatic pressure of 1.5 kbar is required to reach the superconducting state at  $T_c = 2.8$  K.<sup>54,63</sup> This compound triggered particular interest because at ambient pressure no indication of magnetic order could be observed down to lowest temperatures, despite the considerable antiferromagnetic exchange of  $J \approx 250$  K within the triangular lattice.<sup>64</sup>

The transfer integral  $t_1$  of the two molecules composing the dimer is estimated to be approximately 0.2 eV<sup>63,65</sup> and the onsite Coulomb repulsion  $U \approx 2t_1$ .<sup>66</sup> The coupling between the dimers is smaller by a factor of 3 to 6 compared to the intradimer transfer integrals. The effective Coulomb interaction  $U/t$  increases considerably when going from the metal  $\kappa$ -Br to the Mott insulator  $\kappa$ -CN, as summarized in Tab. I. More important, however, is the degree of frustration expressed by the ratio of the transfer integrals, that is  $t'/t \approx 0.42$  and  $0.44$  in the case of the Fermi-liquid  $\kappa$ -Br and the Mott insulator  $\kappa$ -Cl, respectively. For the spin-liquid compound  $\kappa$ -CN, the effective Hubbard  $U$  is larger ( $U/t = 7.3$ ) and most important the transfer integrals  $t'/t = 0.83$  are very close to equality.<sup>39</sup> Similar values have been ob-

TABLE I: Hopping parameters  $t'$  and  $t$  of different  $\kappa$ -phase salts obtained from density functional theory calculations.<sup>39</sup> The ratio  $t'/t$  is a measure of frustration. In all cases the intradimer transfer integral is estimated to  $t_1 = 0.2$  eV and the on-site Coulomb repulsion  $U \approx 2t_1$ .<sup>63,65,66</sup> The Hubbard  $U$  with respect to  $t$  is a measure of the effective electronic correlations.

$\kappa$ -(BEDT-TTF) <sub>2</sub> X	$t'/t$	$U/t$	$t_1$ (meV)	$t$ (meV)	$t'$ (meV)
X=					
Cu[N(CN) <sub>2</sub> ]Br	0.42	5.1	200	78	33
Cu[N(CN) <sub>2</sub> ]Cl	0.44	5.5	200	73	32
Cu <sub>2</sub> (CN) <sub>3</sub>	0.83	7.3	200	55	45

tained from *ab initio* derivations by Nakamura *et al.*<sup>67</sup> For most models and theoretical descriptions, the interaction between BEDT-TTF layers and anions is neglected, however, first-principles density-functional theory calculations recently indicate the importance of donor-anion hydrogen bonding.<sup>68</sup>

Hotta suggested<sup>33</sup> that despite the strong intradimer coupling  $t_1$  quantum electric dipoles are formed on the dimers which interact with each other and thus modify the exchange coupling  $J$  between the spins on the dimers, crucial for the formation of the spin liquid state. Starting with a quarter-filled extended Hubbard model that includes the interaction  $V$  between molecules on the same but also different dimers, she derives an effective dipolar-spin model. The quantum electric dipoles fluctuate by  $t_1$ . For large  $t_1$  a dimer Mott insulator is stable, forming a dipolar liquid, but if  $V$  is large compared to  $t_1$ , charge order emerges (dipolar solid), as sketched in Fig. 2. Similar considerations have been put forward by other groups.<sup>34–36</sup>

Within the dimer model, Imada and collaborators<sup>69</sup> presented an *ab initio* study of  $\kappa$ -phase materials applying a single-band extended Hubbard model. They discovered that charge fluctuations are enhanced by the inter-dimer Coulomb interaction. It is not clear whether the magnetic phase is stable in the presence of charge fluctuations<sup>70</sup> or whether magnetic and ferroelectric order exclude each other.<sup>34</sup> Certainly further experiments are needed before this issue can be resolved.

### III. VIBRATIONAL SPECTROSCOPY

Reflection measurements were performed on as-grown surfaces of single crystals with light polarized along the two principal optical axes, that are  $E \parallel b$  and  $E \parallel c$  in the case of  $\kappa$ -CN and  $E \parallel c$  and  $E \parallel a$  in the case of  $\kappa$ -Cl and  $\kappa$ -Br. Besides regular in-plane experiments, we put particular emphasis on the polarization perpendicular to the conducting BEDT-TTF planes, a direction which couples to the most charge-sensitive infrared-active intramolecular vibrational mode  $\nu_{27}(b_{1u})$ . To this

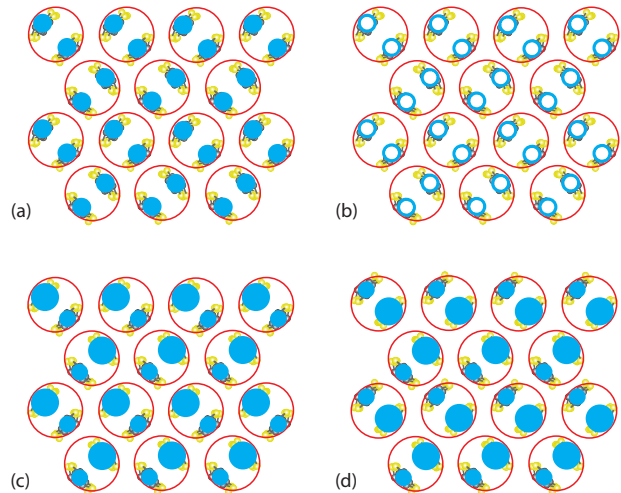


FIG. 2: (Color online) For  $\kappa$ -(BEDT-TTF)<sub>2</sub>X the molecules are arranged in dimers of two BEDT-TTF molecules. Commonly each molecule is assumed to carry equal charge (symbolized by the blue dots); this can be (a) static or (b) fluctuating. Alternatively, it is suggested that the molecules carry unequal charge. This charge disproportionation could form a dipolar solid with the net polarization along (c) vertical or (d) horizontal direction.

end we utilized a Bruker Hyperion infrared microscope attached to the Fourier-transform spectrometer Bruker IFS 66v/s or Vertex 80v.<sup>43,45</sup> The data were collected on the narrow side of the crystals. While for  $\kappa$ -CN all three directions could be well separated, in the case of  $\kappa$ -Br and  $\kappa$ -Cl the data with  $E \parallel b$  and  $E \perp b$  might be a mixture of  $a$ - and  $c$ -directions. The sample was cooled down to  $T = 12$  K by Cryovac Microstat cold-finger cryostat. For the in-plane reflection of  $\kappa$ -CN we also performed temperature-dependent far-infrared measurements using a Bruker IFS 113v equipped with a cold-finger cryostat and in-situ gold-evaporation as reference.<sup>43</sup> In addition the high-frequency optical properties (up to  $35\,000\text{ cm}^{-1}$ ) were determined by spectroscopic ellipsometry at room temperature. In order to perform the Kramer-Kronig analysis using a constant reflectivity extrapolation at low frequencies and temperatures for the Mott insulator  $\kappa$ -CN and  $\kappa$ -Cl, while a Hagen-Rubens behavior was assumed for elevated temperatures and for  $\kappa$ -Br in general.<sup>71</sup>

In order to follow the vibrational modes down to lower temperatures, we additionally conducted optical transmission measurements on a powdered sample. For that purpose single crystals of  $\kappa$ -CN were mixed with KBr and ground to fine powder that was pressed to a 0.35 mm thick disk. The free standing pellet was placed in a He-bath cryostat and cooled down to  $T = 2.5$  K and measured by a Bruker IFS 113v in the mid-infrared range.

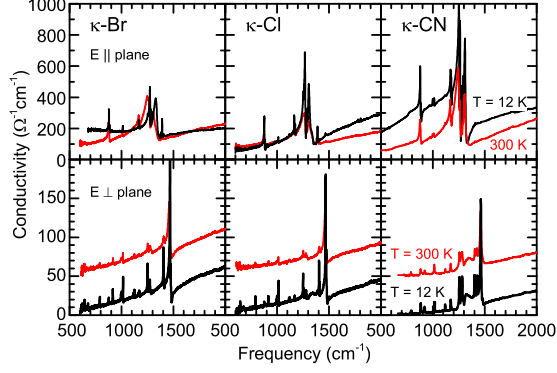


FIG. 3: (Color online) Optical conductivity of  $\kappa$ -(BEDT-TTF) $_2$ X measured within (upper frames) and perpendicular (lower frames) to the BEDT-TTF planes. In the lower row the room-temperature spectra (red lines) are shifted by  $50 (\Omega\text{cm})^{-1}$  with respect to the one measured at  $T = 12$  K (black curves). For  $\kappa$ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$ ]Br and  $\kappa$ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$ ]Cl, the light was polarized  $E \perp b$  and  $E \parallel b$ , while for  $\kappa$ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$  the polarizations were  $E \parallel b$  and  $E \parallel a$ , respectively.

#### IV. RESULTS AND ANALYSIS

In Fig. 3 the frequency-dependent conductivity of  $\kappa$ -Br,  $\kappa$ -Cl and  $\kappa$ -CN is displayed for the mid-infrared range between 500 and 2000  $\text{cm}^{-1}$  measured at room and low temperatures ( $T = 12$  K). The in-plane optical spectra (upper panels) are dominated by the electronic background that changes strongly with temperature, as investigated previously by several groups.<sup>62,72–77</sup> For the out-of-plane conductivity (lower panels) the conductivity is an order of magnitude lower and exhibits no significant temperature dependence in the overall behavior. The vibrational features are well resolved and become narrower upon cooling. The present communication deals only with the analysis and discussion of the molecular vibrations.

##### A. In-plane polarization

Expanded portions of the in-plane conductivity spectra are plotted in Fig. 4 for different temperatures. The most dominant features near 1300  $\text{cm}^{-1}$  are the totally symmetric  $\nu_3(a_g)$  vibrations of the C=C double bonds, which are normally infrared inactive but are activated by electron-molecular vibrational (emv) coupling that involves charge-oscillation between the molecules in each dimer pair. The band is rather broad with a width of approximately 50 to 70  $\text{cm}^{-1}$  that mainly depends on the electronic interaction and thus does not change much with temperature. For the isostructural compounds  $\kappa$ -Br and  $\kappa$ -Cl, the feature is basically centered around the same frequency (1275  $\text{cm}^{-1}$  at room temperature). In  $\kappa$ -Br the maximum weakens and shifts to higher frequen-

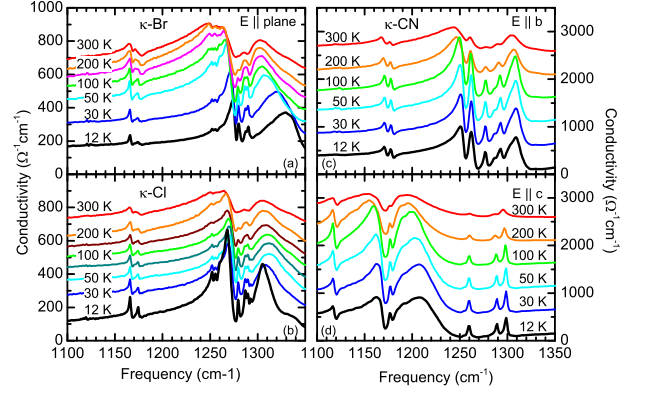


FIG. 4: (Color online) Temperature evolution of the in-plane optical conductivity of (a)  $\kappa$ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$ ]Br (b)  $\kappa$ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$ ]Cl, and (c,d)  $\kappa$ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$  in the range of the emv-coupled  $\nu_3(a_g)$  mode. For clarity reasons the curves are shifted with respect to each other.

cies as the temperature decreases, indicating a weaker electronic coupling, since the interband conductivity decreases due to the shift of spectral weight to the Drude contribution. The opposite behavior is observed in the Mott insulator  $\kappa$ -Cl, where the  $\nu_3(a_g)$  strength grows dramatically and the peak frequency decreases as the mid-infrared peak grows with the formation of the gap.<sup>62,72,73</sup> The four dips between 1377 and 1394  $\text{cm}^{-1}$  belong to a quartet of  $\nu_5(a_g)$  modes and appear as antiresonances within the strong  $\nu_3(a_g)$  mode.<sup>78</sup>

In the case of  $\kappa$ -CN [Fig. 4(c,d)] the vibrational features are quite different for the two polarization within the conducting plane. For  $E \parallel b$  the emv-coupled  $\nu_3(a_g)$  shows up around 1280  $\text{cm}^{-1}$ , while it is shifted to 1180  $\text{cm}^{-1}$  for  $E \parallel c$ , indicating a much stronger emv coupling. This also agrees with the fact, that the optical properties of  $\kappa$ -CN are rather anisotropic compared to  $\kappa$ -Cl.<sup>74,79</sup> It is interesting to see, how the dips (antiresonances) in one case become peaks in the other polarization, and vice versa. Note, the quartet of  $\nu_5(a_g)$  dips within the  $\nu_3(a_g)$  modes is degenerated to a doublet for  $E \parallel c$ . In addition a mode is seen at 1260  $\text{cm}^{-1}$  that does not split for  $E \parallel b$ ; it is also present in the other two compounds and can most likely be assigned to  $\nu_{46}(b_{2u})$  or  $\nu_{29}(b_{1u})$ . In all three compounds we find a double peak at 1166 and 1174  $\text{cm}^{-1}$  which is labeled as  $\nu_{67}(b_{3u})$ . A new Fano-shaped structure occurs around 1118  $\text{cm}^{-1}$  that might be the  $\nu_{47}(b_{2u})$  mode. At lower frequencies the  $\nu_{60}(b_{3u})$  vibrations show up as a strong doublet at around 880  $\text{cm}^{-1}$ ; see Fig. 5. This mode has drawn considerable attention in the past<sup>80–82</sup> and may be regarded as a totally symmetric mode of a distorted BEDT-TTF molecule. For  $\kappa$ -CN it converges to a significant Fano shape in the  $E \parallel c$  polarization. This again indicates the anisotropy of  $\kappa$ -CN and the particularity of the  $c$ -direction in this compound.



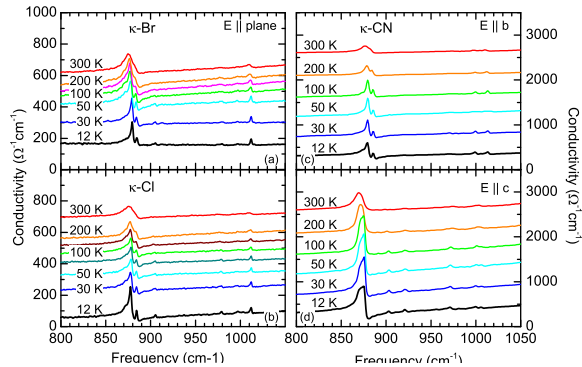


FIG. 5: (Color online) Temperature evolution of the in-plane optical conductivity of (a)  $\kappa$ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$ ]Br (b)  $\kappa$ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$ ]Cl, and (c,d)  $\kappa$ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$  in the range of the  $\nu_{60}(b_{3u})$  mode.

Most important, in no case do we observe a splitting of any of these modes or some appreciable shift beyond the usual thermal dependence.

### B. Out-of-plane polarization

As pointed out by Girlando,<sup>46</sup> Yakushi and collaborators<sup>42,44</sup> the totally symmetric molecular vibrations  $\nu_2(a_g)$  and  $\nu_3(a_g)$  (sketched in Fig. 6) exhibit a strong dependence on ionicity of approximately  $-125 \text{ cm}^{-1}/e$ . Note that the BEDT-TTF molecules are electron donors and thus carry a positive charge of typically 0.5 holes in case of AB $_2$  stoichiometry typically for these compounds.

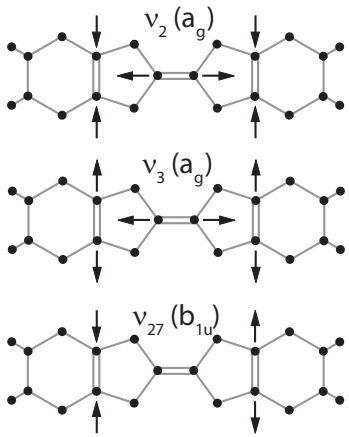


FIG. 6: Sketch of the three most charge-sensitive C=C stretching modes of the BEDT-TTF molecule:  $\nu_2(a_g)$ ,  $\nu_3(a_g)$ , and  $\nu_{27}(b_{1u})$ , according to  $D_{2h}$  symmetry.<sup>46</sup>

But these modes are not well suited for infrared determination of the ionicity because they are strongly affected by the electronic coupling strength and location of the mid-infrared band. The superior local probe of the molecular charge is the antisymmetric stretching mode

$\nu_{27}$  that involves the outer C=C; its eigenfrequency shifts according to<sup>44</sup>

$$\nu_{27}(\rho) = 1398 \text{ cm}^{-1} + 140(1 - \rho) \text{ cm}^{-1}, \quad (1)$$

where  $\rho$  is the site charge. According to the stacking of the BEDT-TTF molecules in the planes, this mode can be best observed perpendicular to the crystal plane.

In Fig. 7 the mid-infrared conductivity ( $E \perp$  planes) of  $\kappa$ -Br,  $\kappa$ -Cl, and  $\kappa$ -CN is plotted for different temperatures; at  $1460 \text{ cm}^{-1}$  we observe the  $\nu_{27}(b_{1u})$  mode exactly where it is expected for half a hole per BEDT-TTF molecule. With decreasing temperature there is a slight hardening of a few  $\text{cm}^{-1}$  and a strong narrowing due to the decrease in interaction with low-lying phonons.<sup>42</sup> The reduced width of the  $\nu_{27}$  feature makes two side bands visible at  $1473$  and  $1478 \text{ cm}^{-1}$ ;  $\kappa$ -CN develops a single satellite at  $1479 \text{ cm}^{-1}$ . The reason lies in the crystallographic inequality among the BEDT-TTF molecules.  $\kappa$ -CN consists of a single conducting layer with two dimers per unit cell, while in  $\kappa$ -Br and  $\kappa$ -Cl the molecules in adjacent layers are tilted in opposite directions as depicted in Fig. 1(c). Similarly the  $\nu_{28}(b_{1u})$  mode shows up as a doublet at around  $1405$  to  $1411 \text{ cm}^{-1}$  for the double layer compounds  $\kappa$ -Br and  $\kappa$ -Cl, while as a single line in  $\kappa$ -CN; the mode slightly softens upon cooling. It is interesting to note the mode at  $1428 \text{ cm}^{-1}$ , which hardens with decreasing temperature, but is present only in  $\kappa$ -CN. Temperature-dependent Raman and infrared experiments on  $\kappa$ -Br confirm our observations: Maksimuk *et al.*<sup>42</sup> could better describe their Raman spectra with two Lorentzians at  $1468$  and  $1475 \text{ cm}^{-1}$ .<sup>83</sup>

### C. Low-temperature anomaly

Thermodynamic,<sup>64,84</sup> transport,<sup>85</sup> dielectric<sup>86</sup> and lattice<sup>87</sup> properties provide evidence for a low-temperature anomaly near  $T = 6 \text{ K}$  that by now has not been explained satisfactorily. Lang *et al.* suggest that charge fluctuations are present at elevated temperatures and around  $6 \text{ K}$  the preformed electric dipoles exhibit some sort of order. This might also influence the magnetic properties. Based on a quarter-filled extended Hubbard model with both electron-electron and electron-phonon interaction taken into account, Mazumdar and collaborators<sup>36</sup> propose a paired electron crystal that includes charge-rich and charge-poor molecules.

In order to experimentally verify whether a charge rearrangement happens around the  $6 \text{ K}$  anomaly, we have performed powder transmission measurements down to temperatures as low as  $2.5 \text{ K}$ . In Fig. 8 the powder absorption spectra of  $\kappa$ -CN are plotted for different temperatures. The peak at  $1464 \text{ cm}^{-1}$  corresponds to the  $\nu_{27}(a_g)$  mode in accord with the reflectivity data presented in Fig. 7; it slightly hardens by approximately  $1 \text{ cm}^{-1}$  and becomes narrower as the temperature is reduced. No significant change is observed when cooled down to  $T = 2.5 \text{ K}$ , giving evidence that no charge order

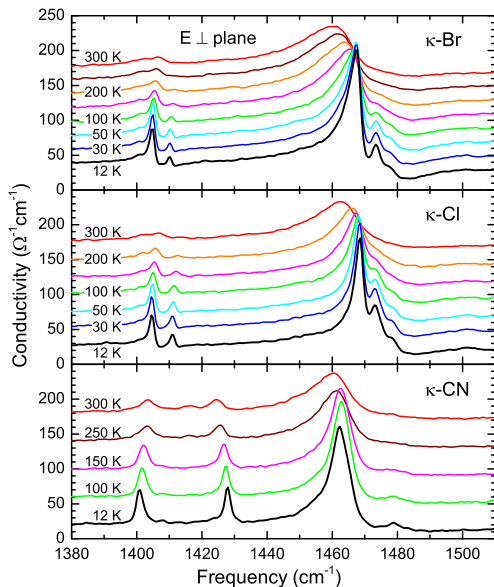


FIG. 7: (Color online) Temperature evolution of the out-of-plane optical conductivity of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br,  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl, and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>, measured at the small side of crystals with the electric field polarized perpendicular to the BEDT-TTF planes. The dominant vibrational mode  $\nu_{27}(b_{1u})$  is a very sensitive local probe of charge per molecule.

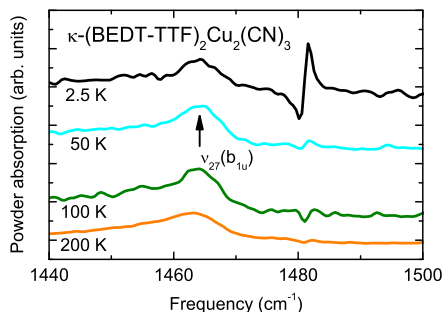


FIG. 8: (Color online) Powder absorption of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> in the range of the C=C molecular vibrations. The  $\nu_{27}(b_{1u}) = 1464 \text{ cm}^{-1}$  mode remains basically unchanged with temperatures, in accord with the reflection data. When cooling down to  $T = 2.5 \text{ K}$  the satellite at  $1480 \text{ cm}^{-1}$  becomes more pronounced and takes a Fano shape. No shift in frequency is observed as the temperature changes. The curves are displaced for clarity reasons.

happens at 6 K or any other temperature. Interestingly, the satellite peak at  $1480 \text{ cm}^{-1}$  becomes continuously stronger as the temperature is reduced from room to helium temperatures; but only below  $T = 6 \text{ K}$  it takes a strong Fano shape.<sup>88</sup> Dielectric measurements<sup>50</sup> give a frequency-independent cusp near that temperature that indicates some dielectric background to which molecular vibrations couple, despite the vanishing dc conductiv-

ity. This behavior has been analyzed elsewhere<sup>79</sup> where charge fluctuations close to a critical point are discussed in more detail.

## V. DISCUSSION

### A. Vibrational features

In none of the in-plane or out-of-plane spectra displayed above we could find indications of charge disproportionation, neither in the metal  $\kappa$ -Br, the Mott insulator  $\kappa$ -Cl above or below the antiferromagnetic ordering, nor in Mott insulator  $\kappa$ -CN, which is supposed to be a spin liquid. Since our data are taken with  $1 \text{ cm}^{-1}$  resolution, we can exclude charge imbalance of more than 3%. For example, a charge disproportionation of  $2\delta = 0.6e$ , as typical for charge-ordered systems such as  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>,<sup>89</sup> results in a splitting of  $80 \text{ cm}^{-1}$ . Nothing like that is found, neither in our present nor previous data,<sup>62</sup> nor in temperature- or pressure dependent Raman and infrared experiments by other groups.<sup>42,77,80,81,90–92</sup> Also complementary methods such as nuclear magnetic resonance (NMR) or x-ray scattering do not evidence charge disproportionation in these  $\kappa$ -phase compounds.<sup>93,94</sup> Pictures like Fig. 2(c,d) with a permanent electric dipole can be ruled out. The experimental findings do not depend on whether the dipoles are oriented or disordered, they just lead to the conclusion that there is no charge imbalance. Either the charge degrees of freedom are not involved in the magnetic and thermodynamic phase transition (which is unlikely) or in a more subtle way beyond the simple arrangements depicted in Fig. 2.

When the temperature is reduced below 6 K, several physical properties exhibit some anomaly indicating a phase transition of unknown origin.<sup>64,84–87</sup> While the change in the lattice properties implies a modification of the frustration parameter  $t'/t$ , x-ray investigations prove that the symmetry does not change, despite the considerable variations with temperature.<sup>41</sup> In particular the hopping parameter  $t'$  in  $b$ -direction increases below 150 K while  $t$  decreases in this temperature range. Furthermore, the interdimer distance becomes smaller at low temperatures and thus the coupling  $t_1$  increases, except for the lowest temperature point at  $T = 5 \text{ K}$ . This is in full agreement with the conclusions drawn from our optical experiments<sup>79</sup> where we identified a shift of the inter-dimer excitations related to that. The  $\kappa$ -CN system is a Mott insulator due to localization of one hole per BEDT-TTF dimer and  $U$  and  $U/t$  become even stronger when cooled to low temperatures.

In order to more quantitatively analyze the  $\nu_{27}(b_{1u})$  mode displayed in Fig. 7, we have fitted the vibrational bands for each temperature. The asymmetry of the features indicates the interaction of the vibrational excitations with the electronic background and Lorentz oscillators yield unsatisfactory fit results. Thus we have utilized the Fano model<sup>95,96</sup> for which the real and imaginary

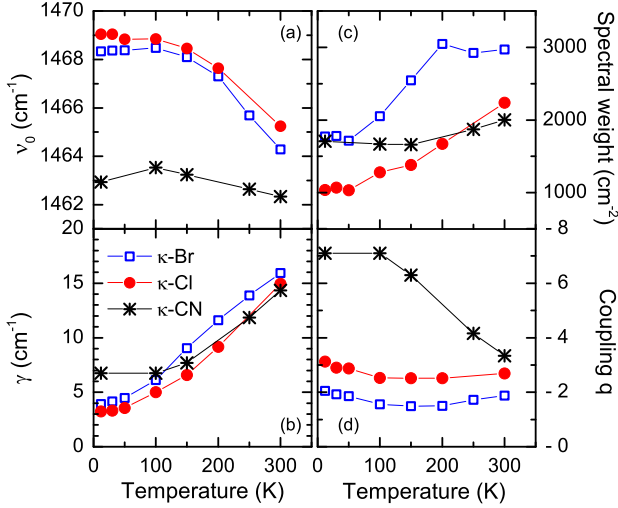


FIG. 9: (Color online) Temperature dependence of the mode parameters obtained from the Fano fit of the  $\nu_{27}(a_g)$  vibrational features of  $\kappa$ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$ ]Br,  $\kappa$ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$ ]Cl, and  $\kappa$ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$ . (a) The resonance frequency  $\nu_0$  of the dominant mode, (b) the damping  $\gamma$ , (c) the mode strength, and (d) the Fano coupling parameter  $q$ .

parts of the conductivity read

$$\sigma_1^{\text{Fano}}(\nu) = \sigma_0 \frac{\gamma\nu [\gamma\nu(q^2 - 1) + 2q(\nu^2 - \nu_0^2)]}{(\nu^2 - \nu_0^2)^2 + \gamma^2\nu^2}, \quad (2a)$$

$$\sigma_2^{\text{Fano}}(\nu) = \sigma_0 \frac{\gamma\nu [(q^2 - 1)(\nu^2 - \nu_0^2) - 2\gamma\nu]}{(\nu^2 - \nu_0^2)^2 + \gamma^2\nu^2}, \quad (2b)$$

where  $\sigma_0$  is the background and  $q$  the phenomenological coupling parameter. Here strong coupling  $q = 0$  yields an antiresonance, no coupling  $q = \pm\infty$  gives a Lorentzian shape; the negative sign indicates that the maximum in  $\sigma_1(\nu)$  occurs at low frequencies while the minimum is located at high frequencies. We define the linewidth  $\gamma = 1/2\pi c\tau$ , the resonance frequency  $\nu_0 = \omega_0/(2\pi c)$ , and the spectral weight  $\int |\sigma_1(\nu) - \sigma_0| d\nu = \nu_p^2/8$ .

For  $\kappa$ -CN we observe a small peak around 1480  $\text{cm}^{-1}$  that calls for a second Fano term with a spectral weight smaller by a factor of approximately 300; at very low temperatures ( $T \approx 2.5$  K), the coupling seems to increase strongly, as seen in Fig. 8. In the case of  $\kappa$ -Br and  $\kappa$ -Cl four modes are needed, with one significantly stronger, but all of them follow a very similar temperature dependence. In Fig. 9 the mode parameters of the dominant peaks for each compound are plotted as a function of temperature. For all three materials the center frequency shifts up as the temperature is reduced to approximately 100 K and then basically saturates. There is a slight downshift observed for  $\kappa$ -Br and  $\kappa$ -CN, but not for  $\kappa$ -Cl. In all cases the spectral weight of the mode is significantly reduced when going to low temperatures [Fig. 9(c)];  $\kappa$ -Br exhibits some anomaly around 200 K which cannot be unambiguously assigned at this point. We are tempted

to relate it to the rearrangement of the ethylene groups that takes place in  $\kappa$ -(BEDT-TTF) $_2X$  salts at elevated temperatures.<sup>97</sup> Interestingly, for  $\kappa$ -CN we observe even a light increase for very low temperatures. If we consider the peak-to-peak difference  $\Delta\sigma$  between the maximum and minimum in conductivity, for all three compounds we find a continuous increase from  $\Delta\sigma = 60 (\Omega\text{cm})^{-1}$  to approximately 150  $(\Omega\text{cm})^{-1}$  as the temperature decreases to 12 K. This is related to the Fano coupling  $q$  and accounts for the asymmetry but also the intensity of the mode and background conductivity.

## B. Fluctuations

Most noteworthy, the damping gets considerably smaller upon cooling with no difference between the metallic or insulating materials as demonstrated in Fig. 9(b); again there seems to be a saturation below 100 K most obvious in  $\kappa$ -CN. The behavior of the curves is monotonous without any discontinuity; the magnitude, however, is higher than expected from the typical narrowing of lattice phonons and molecular vibrations and indicates that charge fluctuations are present at elevated temperatures which are reduced when the temperature is lowered. This behavior is in contrast to the trend commonly observed and most conventional models. Again for  $\kappa$ -CN the behavior is slightly distinct from  $\kappa$ -Br and  $\kappa$ -Cl. It is interesting to go back to Fig. 3 and compare the conductivity at different temperatures. While for  $E \perp$  planes, there is basically no temperature change in the mid-infrared conductivity, we do observe a significant increase for  $E \parallel$  plane at low temperatures. This behavior was investigated in more detail in Ref. 79, where we conclude that fluctuations substantially contribute to the in-plane optical conductivity; these contributions get enhanced at low temperature. Nevertheless, charge fluctuations might also be the reason for the strong change in the damping.

Similar conclusions were drawn by Yamamoto *et al.*<sup>92</sup> from the analysis of the linewidth (5 – 10  $\text{cm}^{-1}$ ) of the Raman active  $\nu_2(a_g)$  mode and the infrared active  $\nu_{27}(b_{1u})$  mode and their temperature dependences; they estimate a charge disproportionation of  $2\delta \approx 0.1e$  for the  $\kappa$ -(BEDT-TTF) $_2X$  salts, which changes only marginally with temperature. Within the uncertainty of this analysis, these findings agree with our conclusions.

If we imagine the electronic charge fluctuating within the dimer and not remaining static as assumed in common models of charge disproportionation, we can quantitatively estimate the fluctuation rate. Depending on the time scale of fluctuations and probe, this results in either a broadening or a splitting of the mode. Kubo suggested a “two-states-jump model” to describe charge to “jump” stochastically between two molecules.<sup>98</sup> Since the vibrational modes in the charge ordered state do have very different strength,<sup>46</sup> the original formula had to be extended to account for the different infrared intensi-

ties, frequency and band-shape of the mode in differently charged molecules.<sup>99</sup> The band-shape function is given by the real part of the following function:

$$\mathcal{L}(\omega) = \frac{\mathcal{F}[(\gamma + 2v_{\text{ex}}) - i(\omega - \omega_w)]}{\mathcal{R}^2 - (\omega - \omega_1)(\omega - \omega_2) - 2i\Gamma(\omega - \omega_{\text{av}})} \quad (3)$$

Here  $\mathcal{F} = f_1 + f_2$ , with  $f_1, f_2$  being the oscillator strengths of the bands of frequency  $\omega_1$  and  $\omega_2$  and halfwidth  $\gamma$ . The charge fluctuation velocity is  $v_{\text{ex}}$ , and  $\Gamma = \gamma + v_{\text{ex}}$  the resulting width, and the abbreviation  $\mathcal{R}^2 = 2\gamma v_{\text{ex}} + \gamma^2$ . Finally, we define the average and weighted frequency,  $\omega_{\text{av}}$  and  $\omega_w$ , by:

$$\omega_{\text{av}} = \frac{\omega_1 + \omega_2}{2}; \quad \omega_w = \frac{f_2\omega_1 + f_1\omega_2}{f_1 + f_2}. \quad (4)$$

If the charge oscillations are slow,  $v_{\text{ex}} \ll |\omega_1 - \omega_2|/2$ , Eq. (3) yields two separated bands centered around  $\omega_1$  and  $\omega_2$ , while if  $v_{\text{ex}} \gg |\omega_1 - \omega_2|/2$ , the motional narrowing will give one single band centred at the intermediate frequency  $\omega_{\text{av}}$ . Finally, when  $v_{\text{ex}} \approx |\omega_1 - \omega_2|/2$  we shall observe one broad band shifted towards the mode with higher oscillator strength. Since we do not see any splitting of the  $\nu_{27}(b_{1u})$  mode and the peaks become narrower as the temperature is reduced, instead of broader as expected from an growing charge disproportionation, the charges are either static or fluctuate with a rate of  $10^{14}$  Hz or more which bring us into the range of electronic transitions.

Another interesting point previously made by Yakushi and collaborators<sup>42</sup> is the eightfold (fourfold) splitting of every internal molecular vibration due to the large unit cell of  $\kappa$ -Br and  $\kappa$ -Cl (in the case of  $\kappa$ -CN). Considering a dimer inside a crystal, these components are divided into  $a_g$  and  $a_u$ , since the two molecules in a dimer are connected by a center of symmetry. In the case of *gerade* molecular modes, the molecules in a dimer oscillate in phase or out of phase, respectively. The interesting point is, that while the  $A_g$  and  $B_{1g}$  modes and the  $B_{2g}$  and  $B_{3g}$  modes in the crystal are nearly degenerate due to the weak interlayer interaction, the degeneracy of the  $A_u$  and  $B_{1u}$ , as well as between  $A_{2u}$  and  $B_{3u}$  is likely to be lifted due to dipole-dipole interaction between the dipoles induced within the layers. This effects accounts for the splitting we observe on various modes in our in-plane and out-of-plane measurements.

It is worthwhile to note, that the electronic coupling between vibrational excitations, either within the dimer or between dimers, happens instantaneously compared to the time scale of the atomic motion (Frank-Condon principle). There is no charge transfer involved that could affect the molecular vibrations nor influence the dielectric properties happening in the radio-frequency range and even lower.

### C. Anisotropy

Let us come back to the remarkable anisotropy observed for  $\kappa$ -CN, as demonstrated in Fig. 4(c,d). There seems to be a much stronger coupling of the  $\nu_3(a_g)$  vibrational modes in *c*-direction compared to the *b*-direction, resulting in a larger downshift due to emv interaction. Since this is the plane the BEDT-TTF molecules are tilted in, it might be related to the coupling of the molecular vibrations to the in-plane excitations. As the temperature is lowered the tilting even increases by approximately  $1^\circ$  which enhances this effect.<sup>41</sup> The major difference, that exists to the  $\kappa$ -Br and  $\kappa$ -Cl properties, with one of them conducting the other insulating, however, implies that simple emv coupling to the conducting electrons is not solely responsible. More likely it is the coupling to the anions that form a two-dimensional network in the *bc*-plane. From x-ray diffraction results,<sup>41</sup> it is known that with decreasing temperatures the  $\text{Cu}_2(\text{CN})_3$  network becomes warped possibly due to the unbalanced interaction with the ethylene groups. A stronger coupling of the anions to one end of the BEDT-TTF molecules also explains why totally symmetric molecular vibrations become infrared active, as in the case of the  $\nu_6(a_g)$  intramolecular vibration. This infers a loss of symmetry (loss of inversion centers) although the translation symmetry is still preserved. It also is consistent with the intriguing results of thermal expansion, that evidence an anomalous behavior around 6 K. From this point of view it is interesting to note, that the dielectric response reported by Abdel-Jawad *et al.* was obtained from experiments perpendicular to the molecular layers.<sup>50</sup> The dielectric constant was found to be rather small ( $\epsilon_1 \approx 10$ ) compared to  $\kappa$ -Cl ( $\epsilon_1 \approx 400$ ).<sup>51</sup> The interaction of positively and negatively charged planes might be the crucial point and requires further considerations. It is of paramount interest to explore the the anisotropy we predict for the dielectric properties within the *bc* plane of the triangular lattice of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>.

## VI. CONCLUSIONS

We have performed comprehensive measurements of the vibrational features of the dimerized  $\kappa$ -(BEDT-TTF)<sub>2</sub>*X* salts, ranging from the superconducting metal  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br to the Mott insulator  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl and the spin-liquid compound  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. Despite the large differences in electronic and magnetic properties, the vibrational features are remarkably similar. In particular focussing on the antisymmetric  $\nu_{27}(b_{1u})$  mode observed in out-of-plane measurements, we can rule out any charge disproportionation within the dimers, and charge fluctuations of a moderate rate. No modification in the charge distribution is observed at any temperature; this also holds for the low-temperature anomaly reported for the spin-liquid  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> around  $T = 6$  K.



This implies that the dielectric relaxation observed in the insulating samples  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> is not due to the formation of paired electron crystals or quantum electric dipoles. We suggest to reconsider the interaction of the molecular layers to the polymeric anion sheet.

### Acknowledgments

We thank N. Drichko, A. Girlando, K. Kanoda, J.-P. Pouget and T. Yamamoto for helpful discussions. D.W.

acknowledges support by the Alexander von Humboldt foundation. The project was supported by the Deutsche Forschungsgemeinschaft (DFG) and by UChicago Argonne, LLC, Operator of Argonne National Laboratory (Argonne). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. We also acknowledge support by the Croatian Ministry of Science, Education and Sports under Grant 035-0000000-2836.

- <sup>1</sup> S. Ishihara, J. Phys. Soc. Jpn. **79**, 011010 (2010).
- <sup>2</sup> N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, and H. Kito, Nature **436**, 1136 (2005).
- <sup>3</sup> P. Monceau, F. Ya. Nad, and S. Brazovskii, Phys. Rev. Lett. **86**, 4080 (2001).
- <sup>4</sup> S. A. Brazovskii, in *The Physics of Organic Superconductors and Conductors*, edited by A. G. Lebed, (Springer-Verlag, Berlin, 2008), p. 313.
- <sup>5</sup> J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Science **299**, 1719 (2003).
- <sup>6</sup> T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura: Nature **426**, 55 (2003).
- <sup>7</sup> K. F. Wang, J. M. Liu, and Z. F. Ren, Adv. Phys. **58**, 321 (2009)
- <sup>8</sup> Y. Tokura and S. Seki, Adv. Mater. **22**, 1554 (2010).
- <sup>9</sup> J. Brink and D. Khomskii, J. Phys.: Condens. Matter **20**, 434217 (2008).
- <sup>10</sup> M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977).
- <sup>11</sup> J.-P. Pouget and S. Ravy, J. Phys. (Paris) I **6**, 1501 (1996).
- <sup>12</sup> M. Dressel, Naturwissenschaften **90**, 337 (2003); *ibid.* **94**, 527 (2007).
- <sup>13</sup> S. Brazovskii, in: *The Physics of Organic Superconductors and Conductors*, edited by A. Lebed (Springer-Verlag, Berlin, 2008), p. 313.
- <sup>14</sup> J.-P. Pouget, Crystals **2**, 466 (2012).
- <sup>15</sup> D. S. Chow, F. Zamborszky, B. Alavi, D. J. Tantillo, A. Baur, C. A. Merlic, and S. E. Brown, Phys. Rev. Lett. **85**, 1698 (2000).
- <sup>16</sup> F. Zamborszky, W. Yu, W. Raas, S. E. Brown, B. Alavi, C. A. Merlic, and A. Baur, Phys. Rev. B **66**, 081103 (R) (2002).
- <sup>17</sup> W. Yu, F. Zhang, F. Zamborszky, B. Alavi, A. Baur, C. A. Merlic, and S. E. Brown, Phys. Rev. B **70**, 121101 (2004); W. Yu, F. Zamborszky, B. Alavi, A. Baur, C. A. Merlic, and S. E. Brown, J. Phys. IV (France) **114**, 35 (2004).
- <sup>18</sup> S. Fujiyama, and T. Nakamura, Phys. Rev. B **70**, 045102 (2004); S. Fujiyama, and T. Nakamura, J. Phys. Soc. Jpn. **75**, 014705 (2005).
- <sup>19</sup> F. Nad, P. Monceau, C. Carcel, and J. M. Fabre, J. Phys. Cond. Matter **12**, L435 (2000); F. Nad, P. Monceau, C. Carcel, and J. M. Fabre, Phys. Rev. B **62**, 1753 (2000); F. Nad, P. Monceau, C. Carcel, and J. M. Fabre, J. Phys.: Condens. Matter, **13**, L717 (2001).
- <sup>20</sup> F. Nad and P. Monceau, J. Phys. IV (France) **12**, Pr9-133 (2002).
- <sup>21</sup> F. Nad and P. Monceau, J. Phys. Soc. Jpn. **75**, 051005 (2006).
- <sup>22</sup> A. Langlois, M. Poirier, C. Bourbonnais, P. Foury-Leylekian, A. Moradpour, and J.-P. Pouget, Phys. Rev. B **81**, 236101 (2010).
- <sup>23</sup> M. Dumm, B. Salameh, M. Abaker, L. K. Montgomery, and M. Dressel, J. Phys. IV (France) **114**, 57 (2004); M. Dumm, M. Abaker, and M. Dressel, J. Phys. IV (France) **131**, 55 (2005).
- <sup>24</sup> K. Furukawa, T. Hara, and T. Nakamura, J. Phys. Soc. Jpn. **74**, 3288 (2005).
- <sup>25</sup> M. Dressel, M. Dumm, T. Knoblauch, and M. Masino, Crystals **2**, 528 (2012).
- <sup>26</sup> M. de Souza, P. Foury-Leylekian, A. Moradpour, J.-P. Pouget, and M. Lang, Phys. Rev. Lett. **101**, 216403 (2008).
- <sup>27</sup> P. Foury-Leylekian, S. Petit, G. Andre, A. Moradpour, and J.-P. Pouget, Physica B **405**, S95 (2010).
- <sup>28</sup> H. Seo, C. Hotta, and H. Fukuyama, Chem. Rev. **104** 5005 (2004); H. Seo, J. Merino, H. Yoshioka, and M. Ogata, J. Phys. Soc. Jpn. **75** 051009 (2006) .
- <sup>29</sup> R. T. Clay, S. Mazumdar, and D. K. Campbell, Phys. Rev. B **67**, 115121 (2003).
- <sup>30</sup> S. Yasin, B. Salameh, E. Rose, M. Dumm, H.-A. Krug von Nidda, A. Loidl, M. Ozerov, G. Untereiner, L. Montgomery, and M. Dressel, Physical Review B **85**, 144428 (2012)
- <sup>31</sup> E. Rose, F. Lissner, T. Schleid, and M. Dressel, to be published.
- <sup>32</sup> T. Takahashi, Y. Nogami, and K. Yakushi, J. Phys. Soc. Jpn. **75**, 051008 (2006).
- <sup>33</sup> C. Hotta, J. Phys. Soc. Jpn. **72**, 840 (2003); Phys. Rev. B **82**, 241104 (2010).
- <sup>34</sup> M. Naka and S. Ishihara, J. Phys. Soc. Jpn. **79**, 063707 (2010).
- <sup>35</sup> H. Gomi, T. Imai, A. Takahashi, and M. Aihara, Phys. Rev. B **82**, 035101 (2010).
- <sup>36</sup> H. Li, R. T. Clay, and S. Mazumdar, J. Phys.: Condens. Matter **22**, 272201 (2010); S. Dayal, R. Clay, H. Li, and S. Mazumdar, Phys. Rev. B **83** 245106 (2011); R. T. Clay, S. Dayal, H. Li, and S. Mazumdar, phys. stat. sol. (b) **249**, 991 (2012).
- <sup>37</sup> The charge-order phenomena in the  $\kappa$ -phase salts with

- an effectively half-filled band are scarce, and only a few salts are reported, such as  $\kappa$ -(BEDT-TTF)<sub>4</sub>-PtCl<sub>6</sub>·C<sub>6</sub>H<sub>5</sub>CN, the triclinic  $\kappa$ -(BEDT-TTF)<sub>4</sub>[M(CN)<sub>6</sub>]-[N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]·3H<sub>2</sub>O and the monoclinic  $\kappa$ -(BEDT-TTF)<sub>4</sub>[M(CN)<sub>6</sub>][N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]·2H<sub>2</sub>O (with  $M = \text{Co}^{\text{III}}$ ,  $\text{Fe}^{\text{III}}$ , and  $\text{Cr}^{\text{III}}$ ) salts [ M.-L. Doublet, E. Canadell, and R. P. Shibaeva, *J. Phys. I (France)* **4**, 1479 (1994); P. Le Maguerès, L. Ouahab, N. Conan, C. J. Gomez-García, P. Delhaès, J. Even, and M. Bertault, *Solid State Commun.* **97**, 27 (1996); L. Ouahab, S. Golhen, T. Le Hoerff, J. Guillevis, L. Tual, N. Hérou, J. Amiel, P. Delhaès, K. Binet, and J. M. Fabre, *Synth. Met.* **102**, 1642 (1999); R. Świetlik, A. Lapiński, L. Ouahab, and K. Yakushi, *Comptes Rendus Chimie* **6**, 395 (2003); R. Świetlik, A. Lapiński, M. Polomska, L. Ouahab, and J. Guillevis, *Synth. Met.* **133**, 273 (2003); R. Świetlik, L. Ouahab, J. Guillevis, and K. Yakushi, *Macromolecular Symposia* **212**, 219 (2004); R. Świetlik, A. Lapiński, M. Polomska, L. Ouahab, and A. Ota, *J. Low Temp. Phys.* **142**, 641 (2006); A. Ota, L. Ouahab, S. Golhen, Y. Yoshida, M. Maesto, G. Saito and R. Świetlik, *Chem. Mater.* **19**, 2455 (2007)]. The structure is rather complex: the phase transition includes the deformation of the molecule and the coupling to the anions; accordingly details of their physical properties and their electronic states are not well-known. Certainly electronic correlations as well as coupling to the lattice are important. Recently, the system  $\kappa$ -(BEDT-TTF)<sub>2</sub>Hg(SCN)<sub>2</sub>Cl was shown to undergo a charge-order transition at 34 K; the metal insulator transition is linked to magnetic order [N. Drichko, R. Beyer, S. Yasin, M. Dressel, J. A. Schlueter, E. I. Zhilyaeva, S. Torunova, and R. N. Lyubovskaya, to be published; S. Yasin, E. Rose, M. Dumm, N. Drichko, M. Dressel, J. A. Schlueter, E. I. Zhilyaeva, S. Torunova, and R. N. Lyubovskaya, *Physica B* **407**, 1689 (2012)].
- <sup>38</sup> T. Mori, H. Mori, and S. Tanaka, *Bull. Chem. Soc. Jpn.* **72**, 179 (1999).
  - <sup>39</sup> H. C. Kandpal, I. Opahle, Y.-Z. Zhang, H. O. Jeschke, and R. Valentí, *Phys. Rev. Lett.* **103**, 067004 (2009).
  - <sup>40</sup> B. J. Powell and R. H. McKenzie, *Rep. Prog. Phys.* **74**, 056501 (2011).
  - <sup>41</sup> H. O. Jeschke, M. de Souza, R. Valentí, R. S. Manna, M. Lang, and J. A. Schlueter, *Phys. Rev. B* **85**, 035125 (2012).
  - <sup>42</sup> M. Maksimuk, K. Yakushi, H. Taniguchi, K. Kanoda, and A. Kawamoto, *J. Phys. Soc. Jpn.* **70**, 3728 (2001).
  - <sup>43</sup> M. Dressel and N. Drichko, *Chem. Rev.* **104**, 5689 (2004).
  - <sup>44</sup> T. Yamamoto, M. Uruichi, K. Yamamoto, K. Yakushi, A. Kawamoto, H. Taniguchi, *J. Phys. Chem B* **109**, 15226 (2005).
  - <sup>45</sup> N. Drichko, S. Kaiser, Y. Sun, C. Clauss, M. Dressel, H. Mori, J. Schlueter, E. I. Zhilyaeva, S. A. Torunova, and R. N. Lyubovskaya *Physica B* **404**, 490 (2009)
  - <sup>46</sup> A. Girlando, *J. Phys. Chem. C* **115**, 19371 (2011).
  - <sup>47</sup> K. Yakushi, *Crystals* **2**, 893 (2012).
  - <sup>48</sup> M. Pinterić, M. Miljak, N. Biškup, O. Milat, I. Aviani, S. Tomić, D. Schweitzer, W. Strunz, and I. Heinen, *Eur. Phys. J. B* **11**, 217 (1999).
  - <sup>49</sup> S. Tomić, M. Pinterić, T. Ivek, K. Sedlmeier, S. Elsässer, R. Beyer, Dan Wu, D. Schweitzer, J. A. Schlueter, and M. Dressel, to be published.
  - <sup>50</sup> M. Abdel-Jawad, I. Terasaki, T. Sasaki, N. Yoneyama, N. Kobayashi, Y. Uesu, and C. Hotta, *Phys. Rev. B* **82**, 125119 (2010).
  - <sup>51</sup> P. Lunkenheimer, J. Müller, S. Krohns, F. Schrettle, A. Loidl, B. Hartmann, R. Rommel, M. de Souza, C. Hotta, J.A. Schlueter, and M. Lang, *Nature Materials*, DOI:10.1038/NMat3400; arXiv:1111.2752.
  - <sup>52</sup> J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, M. H. Whangbo, *Organic Superconductors* (Prentice Hall, Englewood Cliffs, NJ, 1992).
  - <sup>53</sup> N. Toyota, M. Lang, and J. Müller, *Low-Dimensional Molecular Metals*, (Springer-Verlag, Berlin, 2007).
  - <sup>54</sup> U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, H. A. Charlier, J. E. Heindl, G. A. Yaconi, B. J. Love, M.W. Lathrop, J. E. Schirber, D. L. Overmyer, J. Q. Ren, and M.-H. Whangbo, *Inorg. Chem.* **30**, 2586 (1991).
  - <sup>55</sup> A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. Stupka, D. Jung, and M.-H. Whangbo, *Inorg. Chem.* **29**, 2555 (1990);
  - <sup>56</sup> J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrk, K. M. Wathins, J. M. Komers, S. J. Boryschuk, A. V. S. Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung, and M.-H. Whangbo, *Inorg. Chem.* **29**, 3272 (1990).
  - <sup>57</sup> S. Yasin, M. Dumm, B. Salameh, P. Batail, C. Mzire und M. Dressel *Eur. Phys. J. B* **79**, 383 (2011).
  - <sup>58</sup> U. Welp, S. Fleshler, W. K. Kwok, G. W. Crabtree, K. D. Carlson, H. H. Wang, U. Geiser, J. M. Williams, and V. M. Hitsman, *Phys. Rev. Lett.* **69**, 840 (1992).
  - <sup>59</sup> K. Miyagawa, A. Kawamoto, Y. Nakazawa, and K. Kanoda, *Phys. Rev. Lett.* **75**, 1174 (1995).
  - <sup>60</sup> The reports on the magnetic ordering do not agree in all details. Welp *et al.* (Ref. 58) see antiferromagnetic order up to  $T_N = 45$  K and a weak ferromagnetic behavior below  $T_C = 22$  K. NMR experiments, however, only show an antiferromagnetic order at approximately 27 K (Ref. 59). Ishiguro and coworkers report antiferromagnetic resonances and find fluctuations well above 35 K [H. Ito, M. Kubota, Yu. V. Sushko, N. Kojima, G. Saito and T. Ishiguro, *Synth. Met.* **70**, 925 (1995); M. Kubota, G. Saito, H. Ito, T. Ishiguro, and N. Kojima, *Mol. Cryst. Liq. Cryst.* **284**, 367 (1996)]. The temperature dependence of the susceptibility  $\chi(T)$  starts to decrease below 50 K, getting steeper as the temperature is drops further but vanishes only below 25 K, when the antiferromagnetic ground state is completely established (Ref. 57). At higher fields, antiferromagnetic resonance have recently been observed in this range [Á. Antal, T. Fehér, A. Jánosy, E. Tátrai-Szekeres, and F. Fülöp, *Phys. Rev. Lett.* **102**, 086404 (2009)].
  - <sup>61</sup> F. Kagawa, K. Miyagawa, and K. Kanoda, *Nature* **436**, 534 (2005); F. Kagawa, K. Miyagawa and K. Kanoda, *Nature Physics* **5**, 880 (2009).
  - <sup>62</sup> D. Faltermeier, J. Barz, M. Dumm, M. Dressel, N. Drichko, B. Petrov, V. Semkin, R. Vlasova, C. Mézière, and P. Batail, *Phys. Rev. B* **76**, 165113 (2007).
  - <sup>63</sup> T. Komatsu, N. Matsukawa, T. Inoue, and G. Saito, *J. Phys. Soc. Jpn.* **65**, 1340 (1996).
  - <sup>64</sup> Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, G. Saito, *Phys. Rev. Lett.* **91**, 107001 (2003); Y. Kurosaki, Y. Shimizu, K. Miyagawa, K. Kanoda, G. Saito, *Phys. Rev. Lett.* **95**, 177001 (2005).
  - <sup>65</sup> K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi, and G. Saito, *Phys. Rev. B* **38**, 938 (1988).
  - <sup>66</sup> R.H. McKenzie, *Comments Cond. Mat.* **18**, 309 (1998).
  - <sup>67</sup> K. Nakamura, Y. Yoshihide, T. Kosugi, R. Arita, and M.

- Imada, J. Phys. Soc. Jpn. **78**, 083710 (2009).
- <sup>68</sup> P. Alemany, J.-P. Pouget, and E. Canadell, Phys. Rev. B **85**, 195118 (2012)
- <sup>69</sup> H. Shinaoka, T. Misawa, K. Nakamura, and M. Imada, J. Phys. Soc. Jpn. **81**, 034701 (2012).
- <sup>70</sup> L. F. Tocchio, A. Parola, C. Gros, and F. Becca, Phys. Rev. B **80**, 064419 (2009).
- <sup>71</sup> M. Dressel and G. Grüner, *Electrodynamics of Solids* (Cambridge University Press, Cambridge, 2002).
- <sup>72</sup> J. E. Eldridge, K. Kornelsen, H. H. Wang, J. M. Williams, A. V. D. Crouch, and D. M. Watkins, Solid State Commun. **79**, 583 (1991).
- <sup>73</sup> K. Kornelsen, J. E. Eldridge, H. H. Wang, H. A. Charlier, and J. M. Williams, Solid State Commun. **81**, 343 (1992).
- <sup>74</sup> I. Kezsmarki, Y. Shimizu, G. Mihaly, Y. Tokura, K. Kanoda, and G. Saito, Phys. Rev. B **74**, 201101 (2006)
- <sup>75</sup> J. Merino, M. Dumm, N. Drichko, M. Dressel, and R.H. McKenzie, Phys. Rev. Lett. **100**, 086404 (2008).
- <sup>76</sup> M. Dumm, D. Faltermeier, N. Drichko, M. Dressel, C. Mézière, and P. Batail, Phys. Rev. B **79**, 195106 (2009).
- <sup>77</sup> J. J. McGuire, T. Rößm, A. Pronin, T. Timusk, J. A. Schlueter, M. E. Kelly, and A. M. Kini, Phys. Rev. B **64**, 094503 (2001).
- <sup>78</sup> K. Kornelsen, J. E. Eldridge, H. H. Wang, and J. M. Williams, Phys. Rev. B **44**, 5235 (1991).
- <sup>79</sup> S. Elsässer, Dan Wu, M. Dressel, and J. A. Schlueter, arXiv:1208.1664, to be published in Phys. Rev. B.
- <sup>80</sup> J. E. Eldridge, Y. Lin, H. H. Wang, J. M. Williams, and A. M. Kini, Phys. Rev. B **57**, 597 (1998).
- <sup>81</sup> Y. Lin, J. E. Eldridge, J. Schlueter, H. H. Wang, and A. M. Kini Phys. Rev. B **64**, 024506 (2001); J. E. Eldridge, Y. Lin, J. Schlueter, H. H. Wang, and A. M. Kini, Mol. Cryst. Liq. Cryst. **380**, 93 (2002).
- <sup>82</sup> J. L. Musfeldt, R. Swietlik, I. Olejniczak, J. E. Eldridge, and U. Geiser, Phys. Rev. B. **72**, 014516 (2005).
- <sup>83</sup> It is interesting to note that the splitting did no occur in deuterated crystals, indicating the importance of the coupling to the anionic layers by the methyl groups.
- <sup>84</sup> S. Yamashita, Y. Nakazawa, M. Oguni, Y. Oshima, H. Jojiri, K. Miyagawa, and K. Kanoda, Nat. Phys. **4**, 459 (2008).
- <sup>85</sup> M. Yamashita, N. Nakata, Y. Kasahara, T. Sasaki, N. Yoneyama, N. Kobayashi, S. Fujimoto, T. Shibauchi, and Y. Matsuda, Nat. Phys. **5**, 44 (2008).
- <sup>86</sup> M. Poirier, S. Parent, A. Côté, K. Miyagawa, K. Kanoda, and Y. Shimizu, Phys. Rev. B **85**, 134444 (2012).
- <sup>87</sup> R. S. Manna, M. de Souza, A. Brühl, J. A. Schlueter, and M. Lang, Phys. Rev. Lett. **104**, 016403 (2010); M. Lang, R. S. Manna, M. de Souza, A. Brühl, and J. A. Schlueter, Physica C **405**, S182 (2010).
- <sup>88</sup> A similar Fano-shaped resonance at  $987\text{ cm}^{-1}$  becomes very pronounced as the temperature is reduced to  $T = 2.5\text{ K}$ . We assign it to the  $\nu_6(a_g)$  mode that is rather strong in the Raman response but has been observed in infrared spectra previously (Ref. 91). It mainly involved the outer ring and the terminating ethylene groups; implying that the mode is affected by the asymmetric coupling to the anion layers.
- <sup>89</sup> T. Ivek, B. Korin-Hamzić, O. Milat, S. Tomić, C. Clauss, N. Drichko, D. Schweitzer and M. Dressel, Phys. Rev. Lett. **104**, 206406 (2010); Phys. Rev. B **83**, 165128 (2011).
- <sup>90</sup> K. D. Truong, D. Achkir, S. Jandl, and M. Poirier, Phys. Rev. B **51**, 16168 (1995); K. D. Truong, S. Jandl, B. Danilovic, and M. Poirier, Synth. Met. **104**, 157 (1999). K. D. Truong, S. Jandl, and M. Poirier, Synth. Met. **157**, 252 (2007).
- <sup>91</sup> J. E. Eldridge, C. C. Homes, J. M. Williams, A. M. Kini, and M.-H. Whangbo, Spectrochim. Acta, Part A **51**, 947 (1995); J. E. Eldridge, Y. Xie, H. H. Wang, J. M. Williams, A. M. Kini, and J. A. Schlueter, Spectrochim. Acta, Part A **52**, 45 (1996); J. E. Eldridge, Y. Xie, Y. Lin, C. C. Homes, H. H. Wang, J. M. Williams, A. M. Kini, and J. A. Schlueter, Spectrochim. Acta, Part A **53**, 565 (1997).
- <sup>92</sup> T. Yamamoto, K. Matsushita, Y. Nakazawa, K. Yakushi, M. Tamura, and R. Kato (unpublished).
- <sup>93</sup> Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Phys. Rev. B **73**, 140407 (2006).
- <sup>94</sup> K. Kanoda (private communication)
- <sup>95</sup> U. Fano, Phys. Rev. **124**, 1866 (1961).
- <sup>96</sup> A. Damascelli, K. Schulte, D. van der Marel, and A. A. Menovsky, Phys. Rev. B **55**, R4863 (1997).
- <sup>97</sup> J. Müller, M. Lang, F. Steglich, J. A. Schlueter, A. M. Kini, and T. Sasaki, Phys. Rev. B **65**, 144521 (2002).
- <sup>98</sup> R. Kubo, in: *Advances in Chemical Physics*, Vol. 15 (Wiley, New York, 1969), Chap. 6, p. 101
- <sup>99</sup> A. Girlando, M. Masino, S. Kaiser, Y. Sun, N. Drichko, M. Dressel and H. Mori, Phys. Stat. Sol. B **249**, 953 (2012).